Impact of field stress on electrochemical properties of LLZO

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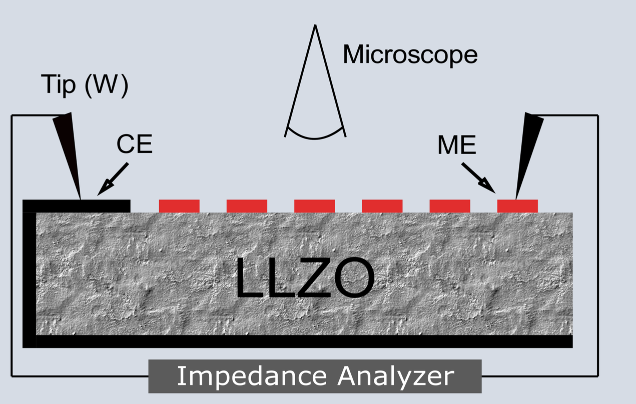
Introduction

Doped $Li_7La_3Zr_2O_{12}$ (LLZO) is a promising candidate for Li electrolytes for all solid-state Li-ion batteries, due to its high ionic conductivity and electrochemical stability [1]. Despite the great research effort focused on LLZO, reliable synthesis of highly conductive garnets remains challenging. Variations in conductivity for nominally equal samples of up to two orders of magnitude are reported in literature [2]. These variations could be connected to fluctuations in stoichiometry caused by the high temperature during synthesis. The relation between conductivity and stoichiometry is essential to get a deeper understanding of the material properties. For these investigations, samples with defined stoichiometry gradients are of great interest.

In this work we pursued to induce compositional changes in Ta-doped LLZO single crystals by applying electric fields with ionically blocking electrodes. Impact of electric fields on electrochemical properties as well as stoichiometry was investigated.
Further we used reactive radio frequency (RF)-sputtering to synthesise reversible thin film electrodes. Crystal structures and elemental compositions of the sputtered materials were investigated by means of X-Ray diffraction (XRD) and Inductively coupled plasma mass spectroscopy (ICP-MS). $Li_4Ti_5O_{12}$ (LTO) and $LiCoO_2$ (LTO) thin-film electrodes were sputtered onto Ta:LLZO single crystals, resulting in all solid state Li-ion cells. These cells were subjected to galvanostatic DC-Cycling, sucessfuly, showing electrochemical energy storage in sputtered all solid state cells.

Analysis techniques

Electrochemical Impedance Spectroscopy (EIS)

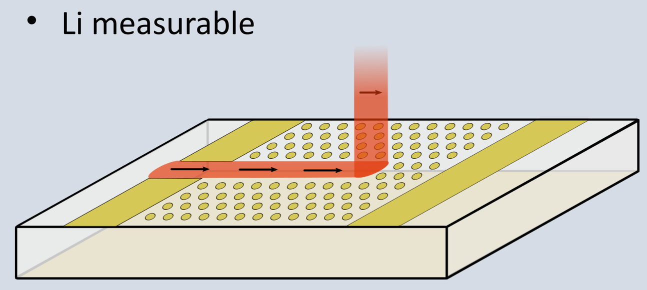


Schematic of microelectrode (ME) measurement setup

- Blocking (Au) electrodes
- Microelectrode (ME) diameter: 100 µm
- Laterally resolved ionic conductivity measurements

Laser Induced Breakdown Spectroscopy (LIBS)

- Direct solid analysis of elemental compositions
- Laterally resolved
- Li measurable



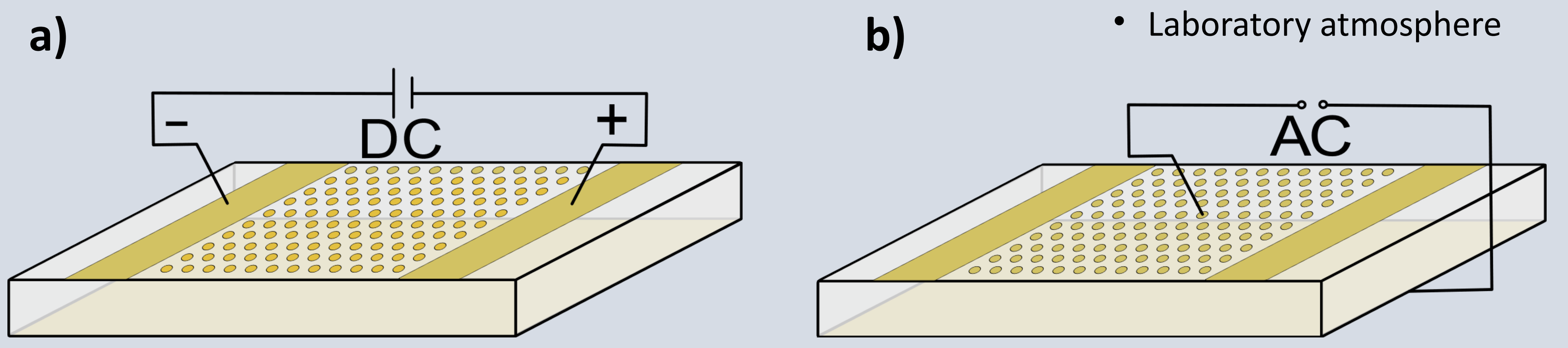
Schematic of a LIBS line scan measurement

Changing stoichiometry and conductivity

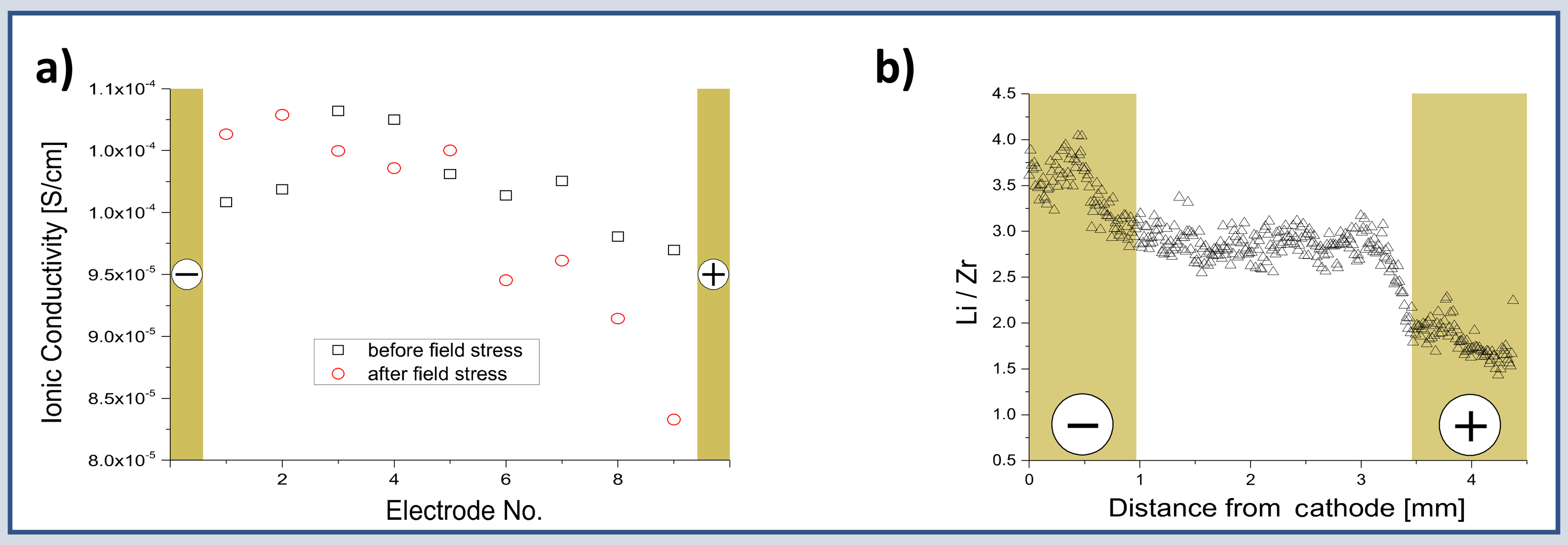
Inducing conductivity and stoichiometry gradients in Ta-doped LLZO single crystals by field stress:

- First Step: Applying electric fields at elevated temperatures for several hours, subsequently cooling down to room temperature. Field still applied until sample has cooled.
- Second Step: Laterally resolved conductivity measurements by means of ME-EIS.

- Electric Field: 10 - 15 V/cm
- Temperature: 300 - 400 °C
- Duration: 12 - 45 h
- ME diameter: 100 µm
- Laboratory atmosphere

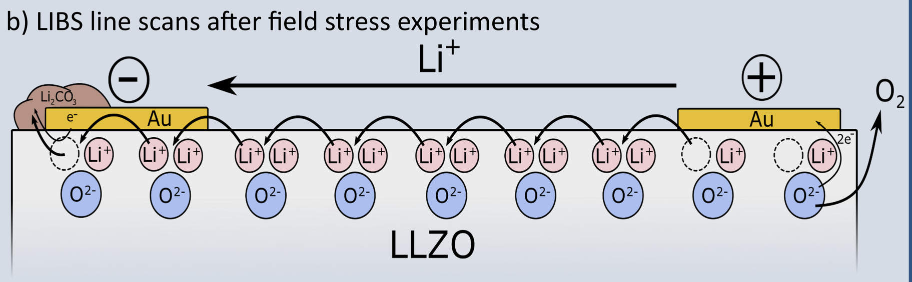


Measurements setup of a) sample polarization by applying DC voltage and b) conductivity profiling by EIS using microelectrodes



Results of a) ME-EIS measurements and b) LIBS line scans after field stress experiments

EIS: **Increased conductivity** next to **cathode** and **decreased conductivity** next to **anode.**
LIBS: Almost **no gradient** in stoichiometry between the stripe electrodes. **Strong stoichiometry variations** at the stripe electrodes **due to formation of Li_2CO_3 and $Li_{7-2x}La_3Zr_2O_{12-x}$.**



Suggested mechanism of decomposition under field stress

Conclusion

- Negative voltages applied via blocking electrodes leads to conductivity changes and decomposition of LLZO below -1 V.
- Sputtering active electrodes on LLZO can be used to obtain all solid state LIBs

Sputtering active electrodes

The device for RF-sputtering was built in-house. Alongside Ar, reactive gases (O_2 and N_2) can be introduced. Wires inside the chamber allow for electrochemical measurements without opening the chamber.

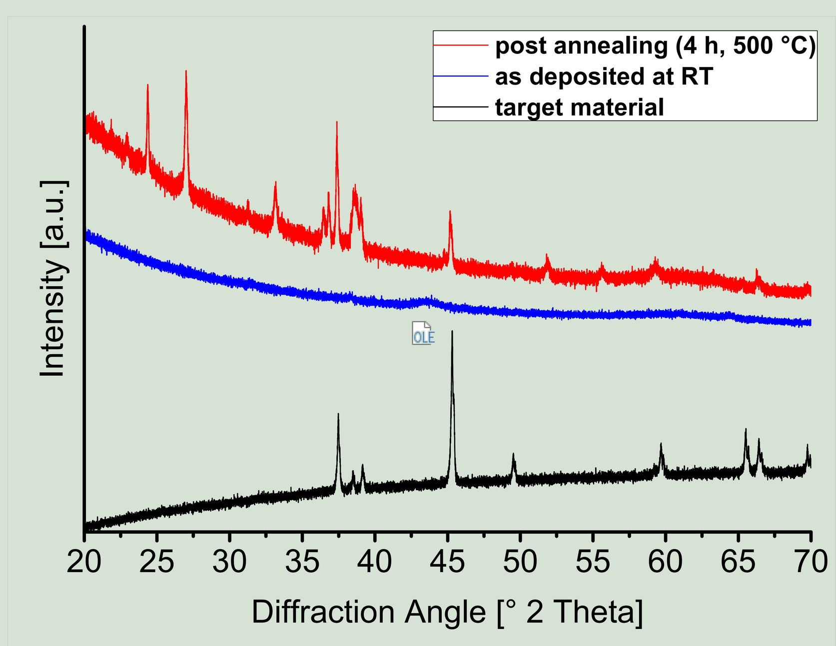
Reactive Sputtering

- Thin films of $LiCoO_2$, $Li_4Ti_5O_{12}$ and other materials for LIBs
- Well defined substrate temperature
- In-house built device allows for in-situ measurements
- All solid state cells

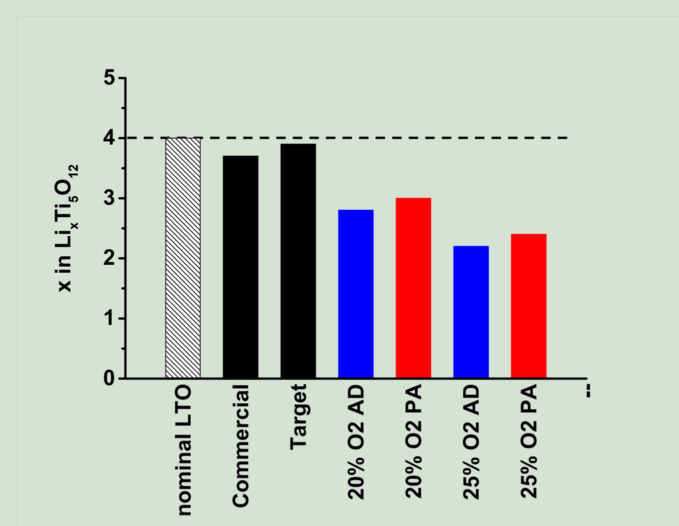
Active thin film electrodes are sputtered on **LLZO** substrates to investigate **interfaces** between these materials.

Characterization

- **Crystal structure** of sputtered thin films via **XRD**
- Elemental **composition** via wet chemical **ICP-MS**

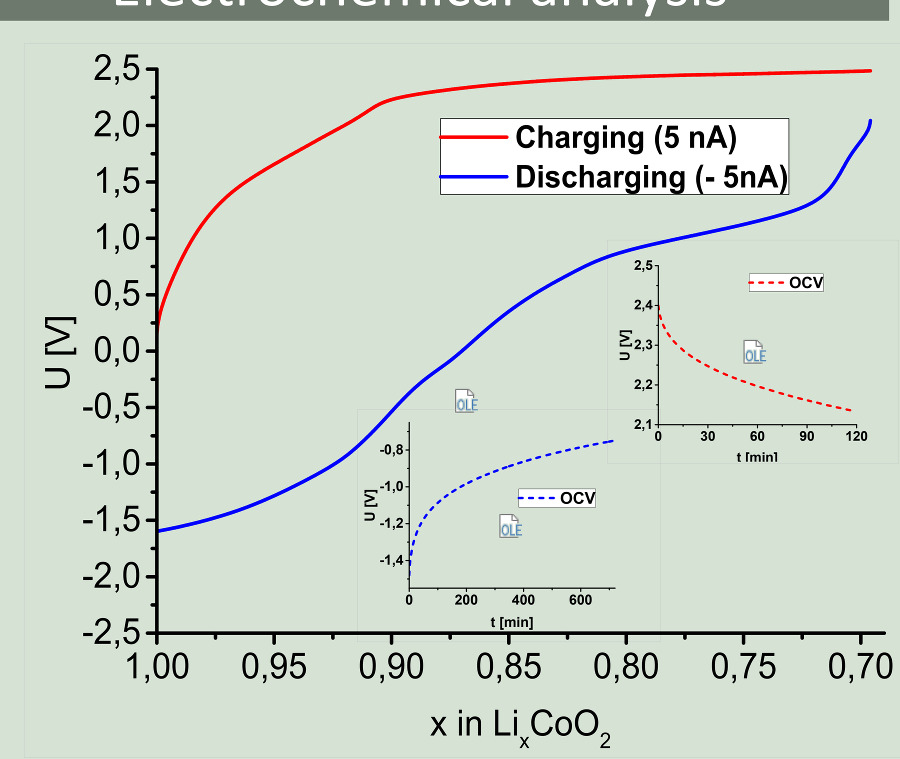


X-Ray diffractogram of a $LiCoO_2$ thin film (500 nm) and the target material. The figure clearly indicates, that the crystallyzation of $LiCoO_2$ requires an annealing step (4h, 500°C) after deposition at RT. The presence of undesired phases is attributed to side reactions with the Si-substrate during annealing.



Results from mass spectroscopy of various LTO samples. Nominal $Li_4Ti_5O_{12}$ films were deposited on YSZ substrates at different O_2 partial pressures. As-deposited and annealed samples were analyzed. Commercial LTO powder and target material were used as reference substances. A general Li-deficiency in sputtered films is apparent.

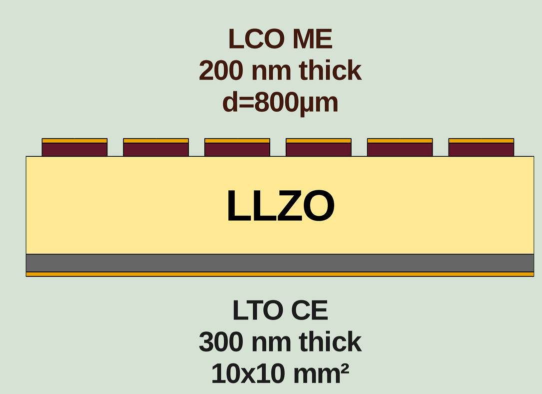
Electrochemical analysis



Voltage profile measured during galvanostatic cycling of a LCO-ME vs. LTO. The profile shows a voltage plateau during charging and discharging at about 2.5 V and 1.2 V, respectively. The results prove, that the tested all solid state cell can be used to reversibly store electrochemical energy. Open circuit voltage was measured after each galvanostatic step (see insets).

All solid state LIB:

- LCO microelectrodes, large LTO counterelectrode
- Multiple „separate" cells on one sample
- Variation of Li-content in ME has small effect on large CE



Schematic of an all solid state cell which was prepared by sputtering LTO and LCO onto a Ta:LLZO single crystal. The sample was annealed twice to achieve crystalline electrode materials.

References:
[1] R. Murugan et al., Angew. Chem. Int. Ed. 46, (2007) 7778–7781.
[2] A. Wachter-Welzl et al., Sol. State Ionics 319 (2018) 203–208.

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